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METHOD FOR TREATING WATER-CONTAINING POLYMER

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Claim

A method for treating a water-containing polymer, characterized in that when a water-containing polymer gel comprising an acrylamide polymer or a copolymer of acrylamide as a main component with sodium acrylate is treated to extract unreacted acrylamide, the extraction is carried out using an aqueous methanol solution as an extracting agent by stirring under such conditions that the average methanol concentration with respect to the total volatile component in the extraction system is in a range of 85-65 wt% and the temperature of the extraction system is 30°C or higher.

Detailed explanation of invention

The present invention relates to a method for extracting unreacted acrylamide monomer in a water-containing polymer comprising acrylamide polymer or a copolymer of acrylamide as a main component with sodium acrylate.

It has been known that a residual monomer can be removed from a water-soluble polymer, which has been prepared by polymerization, by extracting using an organic solvent such as methanol or acetone, which dissolves the monomer in the polymer without dissolving the polymer, but in the case of its industrial application, the extraction was not necessarily easy according to the type of polymer or the content of impurities in the polymer and a complicated operation was required so that effective removal was rather difficult.

The present inventors assiduously studied the treatment method of a water-containing polymer gel comprising an acrylamide polymer or a copolymer of acrylamide as the main component with sodium acrylate in order to remove the aforementioned unreacted monomer and, as a result, it was found that it can be favorably treated under a certain limited condition and the present invention was completed.

Namely, the present invention is a method for treating a water-containing polymer, characterized in that when a water-containing polymer gel comprising acrylamide polymer or a copolymer of acrylamide as a main component with sodium acrylate is treated to extract

unreacted acrylamide, the extraction is carried out using an aqueous methanol solution as an extracting agent by stirring under such conditions that the average methanol concentration with respect to the total volatile component in the extraction system is in a range of 85-65 wt% and the temperature of the extraction system is 30°C or higher.

The present invention uses an aqueous methanol solution having high solubility with respect to acrylamide as an extracting agent in the removal of unreacted acrylamide by treating a water-containing polymer gel, but it was presumed at the beginning that a lower methanol concentration is desirable for the purpose of removal of unreacted monomer. However, it was confirmed that as the methanol concentration decreases, the polymer easily dissolves to raise the viscosity in pores of the polymer and to lower the diffusion velocity of the monomer in the pores, so that it lowers the extraction rate of the extracting agent or the monomer in the inner part of the polymer, conversely as the methanol concentration increases, the monomer does not diffuse since the polymer does not swell and thus the extraction rate of the monomer is lowered.

Then, it was found that in order to optimize the extraction rate of the monomer, the average methanol concentration with respect to the total volatile component of the extraction system must be maintained at a range of 85-65 wt%.

In this case, the total volatile component designates whole volatile components such as the extracting agent comprising methanol and water and water existing in the polymer, etc., and unreacted monomer and catalyst residue, etc., are excluded as so-called nonvolatile components. Further, the average methanol concentration indicates the equalized concentration (the internal and external methanol concentration of the polymer during extraction is different, but the final concentration is equalized by the extraction) of the methanol changed by extraction with the extracting agent, and it can be calculated by various application bases. When the average methanol concentration is beyond the range of 85-65 wt%, the extraction rate lowers as mentioned above and the desired purpose cannot be achieved.

Next, the extraction rate of acrylamide monomer is extremely influenced by the system temperature. Namely, as the temperature increases the extraction rate increases and when the extraction is carried out at 30°C or higher, an extremely favorable extraction in industrial aspect can be carried out. There is also an important point. Namely, since in general, the polymer to be extracted is suspended in a liquid after partly becoming fine particles by stirring, in order to remove this from the extracting agent, a great deal of facility investment is required, and the quality of the recovered polymer is notably degraded by the heat history in the recovery process and in many cases it cannot endure as a coagulant. When extraction is carried out at a temperature of 30°C or higher, however, the water-containing polymer becomes soft and fine suspended matter is adsorbed so that the extraction liquid becomes transparent and the loss of

effective components can be reduced. It is important to maintain the temperature of the extraction system at 30°C or higher, preferably up to 70°C, especially around 50°C.

The present inventors et al. obtained the following information on the methanol extraction treatment of water-containing polymer having a solid concentration of 30% and containing 80 parts (parts by weight, hereinafter same) acrylamide and 20 parts sodium acrylate.

Namely, the polymer having a molecular weight of about 5,000,000-10,000,000 is generally used as a coagulant, but when the water-containing gel was made into a small lump having a diameter of about 3 mm, mixed with water and methanol, stirred at an average water/methanol ratio (weight ratio, hereinafter same) in the system of 30/70 and a total nonvolatile component/total volatile component ratio in the system of 1/10 (thus, the average methanol concentration in the total volatile component became 70%) to extract the residual monomer in the water-containing polymer at 20°C, the amount of nonvolatile component suspended or dissolved in the extraction liquid reached 10-15% of total nonvolatile component and the extraction liquid became an opaque semiturbid liquid. When the extraction liquid was dried at 50°C in vacuo to recover nonvolatile components, it almost did not show coagulation property and the monomer remained in about 10% of the nonvolatile component.

However, as a marvelous fact, when the extraction is carried out at 50°C, the extraction liquid is perfectly transparent and the nonvolatile component in the liquid becomes within 3% of total nonvolatile component in the system. This is due to the polymer in the system becoming soft and readily entering a coagulating state by raising the temperature, and this is a part of the important information of the present invention.

In this case, the water-containing polymer as the starting material contained 3.1% (as pure substance) acrylamide, but when the extraction was carried out at 20°C and after separating the gel and the extracting agent, the polymer was washed with methanol to remove the adhered extracting agent and after dried at 50°C in vacuo, the residual acrylamide in the polymer was 0.4%.

According to the present invention method, it is possible to reduce the residual acrylamide in the polymer to about 0.01% by adding new extracting agent and carrying out the extraction two or three times, but when the extraction is carried out at 30°C or lower, the extraction of residual monomer is practically impossible after doing it twice and it is difficult to make the residual monomer content lower than 0.05%.

This phenomenon is due to the fact that the diffusion velocity of the acrylamide monomer being extracted is extremely slow since the polymer is hard and the pores are small at low temperatures, and it is a similar phenomenon that the polymer becomes a hard solid by dehydration in the extraction system of high concentration, such as a methanol concentration of 90% or higher and almost no monomer is extracted.

On the other hand, it is presumed that in the case of high temperature extraction or extraction at a methanol concentration in the aforementioned range, the polymer is soft and pores in the polymer, formed by extraction of water, are also soft and stretched by impact during stirring to help extraction of the residual monomer.

This novel information becomes an important part of the present invention on monomer removal, and the extraction can be easily carried out industrially because of discovery of this of the novel phenomenon.

Hereinafter, the present invention is explained by application examples and comparative examples.

Application Example 1

333 parts aqueous solution containing 80 parts acrylamide and 20 parts sodium acrylate were mixed with 500 ppm (as ammonia)10% (wt% hereinafter same) ammonia water, 25 ppm (as ammonium persulfate) 1% aqueous ammonium persulfate solution and 25 ppm (as sodium sulfite) 1% aqueous sodium sulfite solution, and N_2 was blown into the solution to polymerize with heat generation to obtain a water-containing polymer.

The residual acrylamide monomer in the polymer was 2.3% in total nonvolatile component.

The water-containing polymer was cut to a diameter of 3 mm or less, mixed with aqueous methanol to adjust the total water/total methanol ratio to 3/7 and the total nonvolatile component/total volatile component ratio to 1/15, extracted for 2 h by stirring at 50°C, washed with 70% aqueous methanol after separating the filtrate, and dried at 50°C in vacuo. The resulting polymer contained 0.04% acrylamide. Further, 3% of total nonvolatile component of treated polymer was leached in the filtrate.

Comparative Example 1

The water-containing polymer (finely cut product) obtained in Application Example 1 was mixed with aqueous methanol to adjust the total nonvolatile component/total volatile component ratio at 1/15 and the total water/total methanol ratio at 1/9, extracted for 2 h at 50°C, washed with methanol water at water/methanol ratio of 1/9 and dried in the same manner as in Application Example 1 to obtain a polymer containing 0.6% acrylamide. Further, 5% of treated total nonvolatile component was leached in the extraction liquid.

Comparative Example 2

The water-containing polymer (finely cut product) obtained in Application Example 1 was mixed with aqueous methanol to adjust the total nonvolatile component/total volatile

component ratio to 1/15 and the total water/total methanol ratio to 3/7 and extracted for 2 h by stirring at 15°C. The polymer was washed with methanol water (methanol 70%) and dried in the same manner as in Application Example 1 to obtain a polymer containing 0.2% acrylamide. Further, 13% of treated nonvolatile component was suspended or leached in the extraction liquid.

Application Example 2

The water-containing polymer (finely cut product) obtained in Application Example 1 was mixed with aqueous methanol to adjust the total volatile component/total nonvolatile component ratio to 1/15 and the total water/total methanol ratio to 3/7, extracted for 2 h by stirring at 50°C, mixed with fresh aqueous methanol to adjust the nonvolatile component/volatile component ratio to 1/15 and the water/methanol ratio to 30/70 after separating the filtrate, and extracted 2 h by stirring at 50°C. Then, the polymer was washed with methanol water at a water/methanol ratio of 3/7 and dried at 50°C in vacuo. The polymer thus obtained contained only 0.009% acrylamide.

Comparative Example 3

A polymer, which was obtained by extracting twice in the same manner as in Application Example 2 except that the total water/total methanol ratio in the two rounds of extraction was adjusted to 1/9, washing with methanol water of water/methanol ratio 1/9 and drying in the same manner as in Application Example 2, contained 0.5% acrylamide.

Comparative Example 4

A polymer, which was obtained in the same manner as in Application Example 2 except that the extraction temperature in the two rounds of extraction in the second extraction was changed to 15°C, contained 0.1% acrylamide.